SUMMARY REPORT

CHLOROPHENOLS

Environment Canada
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PACIFIC & YUKON REGION

ENVIRONMENT CANADA
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CHEMICALS IN THE ENVIRONMENT
PACIFIC AND YUKON REGION

V. CHLOROPHENOLS

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1 INTRODUCTION

This report is one in a series entitled "Chemicals in the Environment - Pacific and Yukon Region" prepared by Environment Canada, Environmental Protection (EP) - Pacific and Yukon Region. The objective of these reports is to provide the technical guidance necessary for: a) the interpretation of environmental quality data on specific chemicals, and b) the assessment of potential impacts resulting from the release of these chemicals into the environment.

The series will focus on both naturally occurring and man-made compounds whose release to the environment is of concern due to their persistence, toxicity and/or bioaccumulative abilities.

These reports discuss highlights of existing environmental quality data for B.C. and Yukon and provide information on environmental dynamics, potential impacts on the environment, and pertinent legislation and guidelines controlling both releases to the receiving environment and environmental quality.

2 USES AND SOURCES OF RELEASE

Chlorophenols are synthetic chlorinated organic compounds whose fungicidal and bactericidal properties have led to diverse uses. They have been used as insecticides; herbicides; slimicides in cooling water systems; and preservatives for wood, paint, leathers and textiles. Several uses of chlorophenols have now been discontinued. Tri- and dichlorophenols have been used as intermediates in the manufacture of chemicals and pesticides (2,4-D). Pentachlorophenol and tetrachlorophenol (2,3,4,6-isomer) are used mainly in wood preservation and protection. More than 90% of pentachlorophenol use in Canada is for wood treatment (1). Agriculture Canada is currently reviewing the registration status of chlorophenols for antisapstain purposes. Regulatory proposals include the registration suspension of chlorophenols as antisapstain chemicals effective December 31, 1988 (2). Environment Canada supports this option.

Pentachlorophenol (PCP), tetrachlorophenol (T_4CP) and their more soluble sodium salts (pentachlorophenate and tetrachlorophenate) are used to make commercial wood treatment formulations. These products also contain lower chlorinated phenols and a number of impurities including chlorinated dioxins (hexa, hepta and octa-isomers), chlorinated furans, chlorinated phenoxyphenols and chlorinated diphenyl ethers (3).

Chlorophenols are applied to wood commercially by various methods depending on the intended use and the degree of protection needed. Short-term wood protection against sapstain and mold fungi for lumber exported overseas is achieved by dipping or spraying, primarily with sodium tetrachlorophenate. Deep penetration for longer term wood preservation (necessary for hydro poles, and railway ties) is achieved by pressure or thermal treatment with pentachlorophenol (4).

Chlorophenols used to formulate these products are imported from the U.S. and France. Approximately 750 metric tonnes of chlorophenol compounds are used annually in B.C. Nearly one half of this amount is used to formulate chlorophenate solutions for use in the B.C. lumber industry for wood protection. Major areas of use in the province include the Lower Mainland, Vancouver Island and the central interior (5).

Commercial formulations commonly used for wood protection in British Columbia include Woodbrite 24, Diatox, Woodsheath, Alchem 4135 and Seabrite. These products contain predominantly sodium tetrachlorophenate in concentrations ranging from 5.4% to 27% (6).

There is no commercial use of chlorophenol wood treatment products in Yukon. However, a survey conducted in 1986 showed that 229.6 litres of pentachlorophenol were used by consumers for external wood treatment (fence posts etc.).

Chlorophenols may enter the environment during the formulation, storage and use of wood treatment chemicals, and also as a result of the disposal of contaminated waste products such as dip tank sludges and wood shavings. Major losses to the environment have occurred through spills; dip tank overflows; and as a result of leaching from treated lumber stored in uncovered and uncontained areas during heavy rainstorm events. A recent EP study of chlorophenol contamination in stormwater discharges from five sawmills and two lumber export terminals in B.C. confirmed that environmental releases from lumber storage yard drainage is substantial. Concentrations in stormwater are dependent on a number of factors, including method of lumber treatment and exposure to rainfall. Concentrations of up to 6600 ug/L total chlorophenols were detected in runoff. Stormwater drainage from storage yards routinely exceeds levels acutely toxic to salmonids (7). Numerous chlorophenate spills have been documented in British Columbia and several of these have resulted in fish kills. Groundwater contamination at one B.C. wood treatment facility has also necessitated extensive clean-up.

Much smaller chlorophenol releases occur as a result of the chlorination of industrial and sewage effluent discharges. Certain chlorinated organics, including lower chlorinated phenols, can be formed by the chlorination of wastes containing aromatic hydrocarbons (8). Chlorophenols have been detected in pulpmill effluents and in nearby receiving environments (9). Chlorophenols and other halogenated phenols have also been detected in water at portable water treatment facilities across Canada (10).

Emissions from municipal incinerators are another possible source of chlorophenol release to the environment. Several isomers including 2,3,4,6-T_4CP and PCP have been detected in fly ash and flue gases. It has also been reported that the combustion of wood can result in the formation of these compounds (11).

3 ENVIRONMENTAL DYNAMICS

3.1 Aquatic Systems

Chlorophenols entering aquatic systems can adsorb to suspended particulates and be deposited in the bottom sediments. However, studies show that greater amounts of PCP are dissolved in the water column than bound to suspended matter (12, 13, 14). PCP is more soluble than many other organic contaminants and may be mobilized in aquatic systems through desorption from sediments.

The alkali salt, sodium pentachlorophenate, is especially soluble in water (4000 mg/L at pH 8) compared to pentachlorophenol (15 mg/L at 20°C). In the alkaline conditions of most natural water systems, pentachlorophenol readily dissociates to form sodium pentachlorophenate. At pH 9.0 virtually all is in the sodium salt form (15).

Under certain environmental conditions chlorinated phenols degrade readily in the aquatic environment, primarily by photolytic and microbial processes. Degradation is favoured in aerobic conditions, warm temperatures, high pH, strong sunlight, high nutrient levels and in the presence of microorganisms. Mono-and dichlorophenols degrade rapidly. Compounds with a higher level of chlorination are more resistant, particularly those with a chlorine atom in the meta-position such as 2,3,4,6-tetrachlorophenol and pentachlorophenol (16, 17, 18, 19). The presence of humic substances in the water column can result in more rapid photolysis of some compounds by causing a photosensitized reaction (20, 21, 22). Also, the presence of chloride ions inhibits the photolysis of PCP but not DCP or TCP (20, 23).

Photolytic degradation in the aquatic environment occurs more rapidly in clear, shallow water than in deeper turbid water (24). Pentachlorophenate degrades much faster than un-ionized pentachlorophenol. Products of photolysis include lower chlorinated phenols, chlorinated catechols, chlorinated benzoquinones, tetrachlororesorcinol, tetrachlorohydroquinone, and dichloromaleic acid. The irradiation of highly concentrated solutions of sodium pentachlorophenate has resulted in the formation of small amounts of octachlorodibenzodioxin (3, 25, 26, 27). Chlorophenol degradation in deeper or turbid waters is primarily by microbial action.

The sediment/water interface is an important site for biodegradation as it is mainly the micro-organisms attached to sediment surfaces and rocks that are responsible for chlorophenol degradation (28, 29). The sediment zone most important for pentachlorophenol biodegradation is the top 0.5 to 1 cm layer (30).

Pentachloroanisole is one of the major products of the microbial degradation of pentachlorophenol in the aquatic environment. This compound is often detected in the sediment and biota in chlorophenol contaminated areas. Due to its low solubility, concentrations in water are usually low (16, 31, 32).

Over a short incubation period (3 days) in estuarine waters, photolysis was the major method of transformation for polychlorinated phenols, while microbial degradation was primarily responsible for the transformation of phenol and monochlorophenol (20).

Ecosystem enclosure studies in the marine environment indicated that in the presence of sunlight, photolysis was the major route of chlorophenol breakdown immediately following PCP exposure. After a 3-5 week acclimation period microbial degradation took over as the major route of breakdown (13, 28, 33).

Despite the potential for chlorophenol degradation in the aquatic environment, contamination may persist in areas receiving high or continuing inputs of these chemicals. Following major chlorophenol spills surface water concentrations may return to near background in a few months or less, while levels in sediment, leaf litter and biota often remain elevated for much longer (12, 14, 34). Elevated chlorophenol levels are commonly detected in anaerobic sediment off wood treatment facilities.

3.2 Soil

The persistence of chlorophenols in soil can range from a few weeks to several years. Factors which influence persistence include; chlorophenol formulation, soil type, organic matter content, moisture content, pH, temperature, aeration and the presence of light. Adsorption and persistence of chlorophenols is favoured in soil with low pH, high pKa, low DO and low organic content (17, 18, 32, 33, 35).

Degradation of chlorophenols in soils occurs primarily as a result of microbial activity. Chlorophenols are broken down by reductive dehalogenation, methylation and ring cleavage. Breakdown products identified in soil include lower chlorinated phenols, chlorohydroquinones, chlorocatechols, chlorobenzoquinones and chloroanisoles. The products of complete degradation are CO_2 and chloride ions (33, 36).

Chlorophenol degradation has been observed in anaerobic soils in the presence of established microbial populations. However, in general, degradation occurs more readily in aerobic soil conditions (18).

4 ENVIRONMENTAL LEVELS

4.1 Aquatic Systems

4.1.1 Water and Sediments.

General

In uncontaminated areas chlorophenol levels are close to or lower than the limits of detection and normally do not exceed the ng/L range in water and low ug/kg concentrations in sediments. However, concentrations several orders of magnitude higher have been reported following spills or in the vicinity of industrial discharges (12, 14, 34). For example, water from a stream which received waste from a wood treatment plant in Pennsylvania, United States contained PCP concentrations of up to 10 mg/L (37). Chlorophenols can attain much higher levels in surface water than many other organic contaminants due to their relatively high solubilities.

PCP and T_4CP concentrations in the mg/kg range have been detected in sediments adjacent to certain industrial facilities, particularly those using chlorophenols for wood treatment (1, 12, 14, 34, 37). Sediment samples collected from Lake Superior in 1978 contained up to 100 mg/kg PCP (dry weight). The average PCP concentration in lake water at this location was 11 ug/L (1).

In areas where spills have resulted in the saturation of soils near riverbanks and lake shores, heavy rainfall can result in long term releases from soils and leaf litter (14, 34, 37). A study of Great Lakes area water systems in 1977 revealed surface water concentrations of up to 23 mg/L PCP following heavy rainfall (1).

British Columbia

Pentachlorophenol, tetrachlorophenol and pentachloroansiole (PCA), a degradation product, have been detected in surface waters and sediments collected off various wood treatment facilities in B.C. A 1979 survey of 11 Vancouver Island and Fraser River sites revealed elevated levels in the vicinity of several sawmills. Surface water concentrations of PCP and/or

T_4CP exceeded 1 ug/L, while levels in sediments exceeded 100 ug/kg off several facilities. Trichlorophenol (TCP) was not detected in water samples or in most sediment samples. The highest chlorophenol concentrations were detected at the following locations (38).

TABLE 1 CHLOROPHENOL CONCENTRATIONS IN THE AQUATIC ENVIRONMENT NEAR B.C. WOOD TREATMENT FACILITIES

LOCATION OF FACILITY	CHLOROPHENOL CONCENTRATION					
	WATER (ug/L)			SEDIMENT (ug/kg)		
	PCP	T_4CP	PCA	PCP	T_4CP	PCA
Burrard Inlet	0.75	1.3	<0.001	< 1-240	< 1-280	<0.1-1.5
Victoria	< 0.01	0.06	0.005	TR-500	9-1600	<0.1-7.6
Nanaimo - Mill #1	TR	0.06	<0.001	< 1-170	15-290	<0.1-17
- Mill #2	3.1	3.3	0.005	< 1-67	9-71	<0.1-1.7
Port Alberni	7.3	0.22	<0.001	< 1-590	54-370	1.9-49

TR = Trace (present but below the level of quantification)

In January of 1986, an EP survey of several wood treatment plants along the lower Fraser River indicated environmental levels of chlorophenols were generally lower than those reported for the 1979 survey. The highest concentrations detected in the waters off these facilities were 0.09 ug/L PCP and 0.1 ug/L T_4CP. The highest concentrations detected in sediments were 107 ug/kg PCP and 63 ug/kg T_4CP. Surface waters and sediments at most sites did not contain levels of either compound exceeding 0.02 ug/L or 15 ug/kg, respectively (39).

Water samples collected near Mitchell Island (located in the North Arm of the Fraser River) in 1984/85 by Westwater Research showed that peak chlorophenol concentrations, which occur periodically, could be missed by typical grab sampling methods. Concentrations of over 10 ug/L were occasionally detected. Several wood treatment facilities are located in the vicinity of Mitchell Island. A recent EP study showed that peak loading to the environment from lumber storage yard drainage occurs during heavy rainfall (7). Westwater Research has also reported success using leeches as *in situ* monitors of chlorophenol bioavailability in the Fraser River (40, 41).

Sediment samples collected by EP at a number of sites in the lower Fraser River, Vancouver Harbour, Victoria Harbour and Esquimalt Harbour,

between 1983 and 1985 revealed low chlorophenol levels (T_4CP and PCP <15 ug/kg) at almost all sites. Maximum levels of 78 ug/kg T_4CP and 216 ug/g PCP were detected (39). Most of these sites were not located near wood treatment facilities.

Sediment samples collected in 1985 at Sturgeon Bank near the Iona Island sewage treatment plant discharge contained maximum levels of 10 ug/kg PCP and 13 ug/kg T_4CP. Samples collected at sites distant from the sewage channel did not contain more than 1 ug/kg of either compound (39).

The once heavily industrialized False Creek area in Vancouver has undergone extensive redevelopment. Sediments collected from this area in 1982 generally contained low levels of T_4CP and PCP. Maximum concentrations of 70 ug/kg T_4CP and 89 ug/kg PCP were detected in samples from the east basin near the former site of a wood treatment facility (42). Dredging has resulted in extensive sediment removal from some parts of False Creek since that time. There is no information on current levels of chlorophenols in False Creek sediments.

Low concentrations of PCP, T_4CP, TCP, DCP and other chlorinated phenols (chlorinated catechols and chlorinated guaiacols) were detected in water and sediments collected adjacent to both coastal and inland pulp mills in B.C. However, due to the ubiquity of PCP and T_4CP it was concluded that the pulp mills were not the major source of these compounds (9).

Very high chlorophenol levels have been detected in certain B.C. water systems following major spills.

In 1984, a major release of sodium tetra- and pentachlorophenate (41,000 litres of 2% solution) from a storage tank at a chemical plant in Surrey resulted in a massive fish kill. Immediately after the release water from the ditch receiving the spill contained over 1000 mg/L chlorophenols (43). A creek downstream contained up to 11.6 mg/L in the water and up to 1540 ug/kg (total penta- and tetrachlorophenol) in sediments. However, water concentrations dropped to 406 ug/L the following day due to flushing and clean-up measures. Lower levels of chlorophenol contamination were present in water systems farther downstream and ultimately in the marine environment many kilometers away (44). No damage to the marine environment was observed. Remedial and clean-up measures succeeded in reducing the spread of contamination but water and sediment chlorophenol levels in the ditch remained elevated over many months. Chlorophenol levels in water and

sediment from downstream sites decreased significantly over an eight month period.

Following a 1985 chlorophenate spill at a wood treatment facility at Elk Falls, water from the spill area contained 430 ug/L PCP and 1280 ug/L T_4CP, while sediments contained 2010 ug/kg PCP and 5210 ug/kg T_4CP (45).

Chlorophenols are not used commercially in Yukon and, therefore, no environmental monitoring for these chemicals has been conducted.

4.1.2 Aquatic Organisms.

4.1.2.1 Uptake and elimination. Chlorophenols are readily accumulated by many species of aquatic organisms even when present at low environmental concentrations. However, in general, bioconcentration factors are lower for chlorophenols than for certain other chlorinated organic contaminants such as PCB and DDT (12, 15, 46).

Certain environmental factors affect the rate at which chlorophenols are accumulated by aquatic organisms. Low temperatures result in slower rates of chlorophenol uptake and elimination. PCP uptake in goldfish decreases with increasing pH due to the tendency for PCP to be in the less biologically available dissociated or ionized form at higher pHs (47, 48, 49, 50, 51). An important factor in determining the rate of chlorophenol uptake in crustaceans is the stage in the molt cycle at which exposure occurs. PCP is more readily accumulated immediately after molt than in the intermolt stage (52).

Laboratory studies indicate that the major route of chlorophenol uptake in aquatic organisms is from water rather than from food (53, 54). Some researchers suggest that uptake from the food chain becomes important only when food organisms contain mg/kg levels of chlorophenols (53). Biomagnification of chlorophenols through the food chain is minimal. Higher trophic level predator species do not contain higher concentrations than the primary forage species (53).

Chlorophenols in aquatic organisms are detoxified and eliminated by conjugate (sulphate or glucuronide) formation rather than by decomposition. When removed from the source of contamination, the rate of elimination from most species is quite rapid. The half-life of PCP in fish tissues and organs ranges from one day to more than one week. Interspecific differences in

clearance rates may be partly due to the method of elimination, which may be via branchial, biliary and/or renal excretion (46, 54, 55, 56, 57, 58).

Pentachloroanisole (PCA), which is present in the environment as a degradation product of PCP, is rapidly accumulated by aquatic organisms and has a significantly longer biological half-life than does PCP. Half-lives of several days were reported for PCA in various tissues of rainbow trout, compared to several hours for PCP (59).

4.1.2.2 Levels in Aquatic Organisms.

General

Information on levels of chlorophenols in aquatic organisms is quite limited with most of the available information pertaining to PCP.

Concentrations of several ug/kg PCP and PCA have been detected in biota from industrialized areas (Table 2).

Fish exposed to PCP in a spill situation rapidly accumulate PCP but concentrations usually return to normal after several months as ambient water concentrations decline. Concentrations of up to 200, 40 and 12 mg/kg (wet weight) were detected in the liver, gill and muscle tissue of fish from a creek in Mississippi, U.S.A. following a PCP spill, but concentrations declined to background (< 50 ug/kg) within 10 months (14).

Chlorophenols concentrate mainly in the liver, gall bladder, digestive tract and gills of fish. Muscle tissue normally contains much lower levels (26, 55, 60, 63). Particularly high levels have also been detected in the Bajanus organ in clams (60) and the hepatopancreas in crabs (64, 65).

British Columbia

Available information on chlorophenol levels in B.C. biota is limited to the Fraser River and other south coastal areas near wood treatment facilities and pulp mills.

From 1973 to the present, several species of fish have been collected throughout the Fraser River and analyzed for chlorophenols. Chlorophenols were generally detected with greatest frequency and at the

TABLE 2 CHLORINATED PHENOLS AND ANISOLES IN AQUATIC BIOTA FROM INDUSTRIALIZED AREAS

LOCATION	SPECIES	CONCENTRATION (ug/kg wet weight)	REF.
Galveston Bay, Texas	Oysters	PCP - 3.4 to 8.3 $\bar{x}$ = 5.3	60
Tokyo Bay, Japan	Oysters	PCP - 2 PCA - 20 TCA - 3	61
Lake Ontario	Salmonids (6 species)	PCP $\bar{x}$ values < 1 to 24	53
Lake Superior	fish (3 species)	PCP - 20 to 1000	1
St. Johns and St. Croix Estuary	fish	PCP - < 0.5 to 40	60
Canagagique Creek Ontario	fish (5 species)	PCP - < 2 - 170 TTCP - < 2 - 112 TCP - < 2 - 67	62
	clam (including shell)	PCP - 2 - 7 TTCP - 2 - 19 TCP - 4 - 22	
	snail (including shell)	PCP - 54 TTCP - 14 TCP - 12	
	leech	PCP - 58 - 2798 TTCP - 14 - 1479 TCP - 251 -25471	
	Insect larvae (5 species)	PCP - 2 - 54 TTCP - < 2 - 27 TCP - 9 - 46	
	Frogs (2 species)	PCP - < 2 - 37 TTCP - < 2 - 26 TCP - 2 - 194	

highest concentrations in the heavily industrialized lower reaches of the river, particularly in the North Arm off Mitchell Island. This finding can be explained by the presence of several wood treatment facilities in this area. Elevated chlorophenol levels have been detected in biota (and in water and sediments) collected near several B.C. wood treatment facilities in the Fraser River, and elsewhere in southern B.C., including Vancouver Island (38, 39).

Fish collected from upstream areas of the Fraser River, and in areas not receiving continuing industrial inputs of chlorophenols, normally contained T_4CP and PCP at concentrations below or close to the detection limits (< 1- to 20 ug/kg). T_4CP and PCP were frequently detected in fish from the lower reaches of the Fraser River. Mean levels of 40 to 90 ug/kg were detected in various species collected in backwater slough areas. In some species, such as sculpin, T_4CP and PCP concentrations in whole fish and muscle tissue sometimes exceeded 100 ug/kg (with mean levels of over 50 ug/kg) in the vicinity of certain wood treatment facilities (even nigher concentrations have been reported by Hall et al. (66) for starry flounder). Significantly higher levels have been detected in liver tissue from sculpin (up to 2100 ug/kg PCP and 1600 ug/kg T_4CP) (38).

Trichlorophenol (TCP) was detected in very few B.C. fish. Most surveys have failed to detect dichlorophenol (DCP) in both fish and water, however, some of the larger fish collected in the North Arm of the Fraser River in 1984 contained 3,4-DCP concentrations exceeding those of PCP and T_4CP (67). This finding is now being further investigated. Elevated DCP levels (2,6-; 2,4- and 3,4- isomers) have also been detected in fish from Canagagique Creek in Ontario, total DCP levels of up to 1693 ug/kg were reported (62).

Limited information on chlorophenol levels in B.C. invertebrates indicates that T_4CP and PCP are normally present at concentrations below or close to detection limits (< 1 to 10 ug/kg). Somewhat higher levels have been detected in crabs (up to 20 ug/kg T_4CP; 17 ug/kg PCP) and mussels (up to 690 ug/kg T_4CP; 20 ug/kg PCP) collected near certain wood treatment facilities in southern B.C. (38)

Elevated levels (up to 1700 ug/kg T_4CP in polychaetes) have also

been detected in benthic invertebrates collected near Barnston Island in the Main Stem of the Fraser River and off Queensborough in the North Arm (68).

Following a major chlorophenate spill into a creek in the Surrey area in 1984, elevated levels of chlorophenols were detected in invertebrates collected in the Boundary Bay area downstream. Crabs collected immediately following the spill contained 67-116 ppb total chlorophenols, while oysters contained 171-563 ppb (44) and clams contained 83-108 ppb. DFO closed the area for crab and oyster harvesting on April 12, 1984. However, approximately three months later, most crab, clam and oyster samples contained non-detectable or trace concentrations. Consequently, commercial and sport harvesting of crab was reopened.

In 1985, very high PCP and T_4CP concentrations were detected in various invertebrates (up to 4560 ug/kg PCP; 3530 ug/kg T_4CP) and in algae (3300 ug/kg PCP; 800 ug/kg T_4CP) collected in the vicinity of a wood preservative spill at Elk Falls on Vancouver Island. Algae and invertebrates collected from control sites in Campbell River contained non-detectable or trace concentrations of these compounds (42).

Low levels of chlorinated phenols (PCP, T_4CP and TCP) and other chlorinated phenols (chlorinated catechols and chlorinated guaiacols) have been detected in fish and invertebrates collected in the vicinity of B.C. pulp mills. However, it was concluded that the pulp mills were not the major source of PCP and T_4CP (9).

4.1.2.3 Toxicity. Chlorophenols at ug/L concentrations may affect the survival, growth, metabolism and reproduction of aquatic organisms. Acute and chronic toxicity information for various species of aquatic organisms is presented in Tables 3(i) and 3(ii).

The major toxic action of chlorophenols is the uncoupling of oxidative phosphorylation but a number of other physiological effects, including interference in enzyme activity (69, 70), have been observed. Other effects of chronic chlorophenol exposure include; decreased shell deposition (64), inhibition of limb regeneration (71), increased feeding activity (72), decreased ability to clear bacterial infections (73), decreased growth (food conversion efficiency) (74, 75, 76, 77, 78, 79)

TABLE 3 TOXICITY OF CHLOROPHENOLS TO AQUATIC ORGANISMS

1) Invertebrates

SPECIES	COMPOUND	EXPOSURE TIME	CONCENTRATION (ug/L)	EFFECT [1]	REF.
Eastern oyster					
- embryo	Na-PCP	48 hr	40	EC_{50} - causes abnormal development	99
Grass shrimp					
- 24 hr old	Na-PCP	96 hr	649	LC_{50}	91
- intermolt	Na-PCP	throughout molt cycle	1000	- deterioration of midgut, hindgut, hepatopancreas and gill	91
- adult	Na-PCP	96 hr	436 - 2734	LC_{50}	90
Palaemonetes varians	Na-PCP				
- adult		96 hr	5090	LC_{50}	90
- larvae		96 hr	363	LC_{50}	90
Palaemon elegans	Na-PCP				
- adult		96 hr	10,390	LC_{50}	90
Crangon crangon	Na-PCP				
- adult		96 hr	1790	LC_{50}	90
Planktonic copepod	Na-PCP				
- *P. coronatus*		96 hr	68	LC_{50}	72
Macrobenthic Community	Dowicide* G-ST	13 wks	1.8	- no effect observed	81
			15.8 & 16.1	- decreased number of individuals of certain species with molluscs being the most sensitive	81
Meiobenthic nematodes	Dowicide* G-ST	9 wks	76	- increase biomass and density	80
			161 & 622	- decrease biomass and density	80
				- changes in species composition and feeding	

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TABLE 3 TOXICITY OF CHLOROPHENOLS TO AQUATIC ORGANISMS

i) Invertebrates
(Continued)

SPECIES	COMPOUND	EXPOSURE TIME	CONCENTRATION (ug/L)	EFFECT	REF.
Cypris subglobosa	PCP	96 hr	6560	LC_{50}	100
	Na-PCP	96 hr	4410	LC_{50}	100
Freshwater pulmonate snail	PCP	96 hr	160	LC_{50}	86
	Na-PCP	96 hr	190	LC_{50}	86

ii) Fish

SPECIES	COMPOUND	EXPOSURE TIME	CONCENTRATION (ug/L)	EFFECT	REF.
Steelhead trout					
- 10 wk old fry	Purified PCP	96 hr	66	LC_{50}	85
- embryo		72 days (beginning 24 hrs after fertilization)	14	- threshold for chronic toxic effects	85
- embryo	Na-PCP	1 wk (beginning 15 min. after fertilization)	300	- 100 % mortality	76

CONTINUED...

TABLE 3 TOXICITY OF CHLOROPHENOLS TO AQUATIC ORGANISMS

ii) Fish
(Continued)

SPECIES	COMPOUND	EXPOSURE TIME	CONCENTRATION (ug/L)	EFFECT	REF.
Steelhead trout					
- embryo/alevin	Na-PCP	1 mnth	180	- 100 % mortality primarily before hatch	76
		1 mnth	50 - 80	- 100 % mortality primarily after hatch	76
- alevins	Na-PCP	12 hrs	300	- 100 % mortality	76
		24 days	40	- 76 % mortality (3 mg O_2/L)	76
				- 80 % mortality (5 mg O_2/L)	76
		41 days	40	- 79 % mortality (5 mg O_2/L)	76
				- 24 % mortality (10 mg O_2/L)	76
Rainbow trout	Na-PCP	4 wks	10	- threshold for decreased production (at 20°C)	75
			20	- threshold for decreased production (at 10°C)	75
	Na-PCP	96 hr	230	LC_{50}	84
	Woodbrite* 24	96 hr	400	LC_{50}	84
	Na-PCP	96 hr	47 - 106	LC_{50} (varies with pH and temperature)	95
Coho salmon	Na-PCP	96 hr	32 - 92	LC_{50} (varies with pH and temperature)	95
Sockeye salmon	Na-PCP	96 hr	50 - 130	LC_{50} (varies with pH and temperature)	95
- underyearling	Na-PCP	96 hr	63	LC_{50}	74
			1.74	EC_{50} (affecting growth rate)	74
			1.80	EC_{50} (affecting food conversion)	74
Fathead minnows					
- 30 to 35 days old	PCP	96 hr	220 - 230	LC_{50}	101
		192 hr	200 - 220	LC_{50}	101
	2,4-DCP	96 hr	8200 - 8300	LC_{50}	101
		192 hr	6500	LC_{50}	101

CONTINUED...

TABLE 3 TOXICITY OF CHLOROPHENOLS TO AQUATIC ORGANISMS

ii) Fish
(Continued)

SPECIES	COMPOUND	EXPOSURE TIME	CONCENTRATION (ug/l)	EFFECT	REF.
Fathead minnows					
- 30 to 35 days old	2,4,6-TCP	96 hr	8600 - 9700	LC_{50}	101
		192 hr	5800 - 6400	LC_{50}	101
- 2 weeks old	Dowicide* EC-7	90 day	up to 139	- no effect on growth or survival	
	PCP (tech. grade)		$\geq$ 13	- reduced growth	98
			$\geq$ 27	- reduced survival and growth	98
	Purified PCP		85	- no effect on survival	98
Sheepshead minnow	PCP	2 wks	392	LC_{50}	99
		6 wks	223	LC_{50}	99
	Dowicide* G	2 wks	516	LC_{50}	99
Largemouth bass					
- 14 & 28 days old	Purified PCP	96 hr	285	LC_{50}	102
- 1 & 2 years old	Purified PCP	96 hr	194	LC_{50}	102
Zebrafish	Na-PCP	96 hr	1130	LC_{50}	84
Flagfish	Na-PCP	96 hr	1740	LC_{50}	84

[1] LC_{50} - Concentration at which 50% of the test population dies within specified exposure time
EC_{50} - Concentration at which 50% of the test population exhibits the stated toxic effect within specified exposure time
* Tradenames for chlorophenol based wood treatment products

interference with nerve impulse conduction (80), and decreases and alterations in community structures and populations of certain invertebrate species (72, 81, 82, 83, 84, 85).

Organisms exposed to chlorophenols often exhibit a variety of symptoms including abnormal swimming, excessive mucus secretion, hemorrhaging, loss of equilibrium and an altered respiration rate (86, 87).

Lethal concentrations of PCP for various species of fish range between 0.05 and 1 mg/L. Chronic effects often occur at 1/10th to 1/20th of the 96 hour LC_{50} concentration. Significant interspecific differences in sensitivity to chlorophenols have been observed in aquatic organisms. Size, age and genetic variations may account for some of these differences (84).

Mollusc and salmonid species are particularly sensitive to chlorophenol poisoning. Also, early life stages of invertebrates are often more sensitive than adults (88). Some studies indicate that adult crustaceans are more tolerant to chlorophenols than are adult fish, however, this may not be true of all species (89). The sensitivity of crustaceans to chlorophenols varies with the molt cycle due to changes in the permeability of the cuticle. Increased chlorophenol uptake and more pronounced toxicity are usually observed after molt occurs (89, 90, 91).

Environmental factors such as temperature, pH, dissolved oxygen, salinity and water hardness (88) are important in determining the toxicity of environmental contaminants. The toxicity of chlorophenols usually increases with increasing temperature (75, 88) and low dissolved oxygen content (92). This is probably due to accelerated metabolic and respiratory rates which result in an increased rate of uptake. Chlorophenols are also more soluble in water at higher temperatures. Low pH levels increase the toxicity of chlorophenols due to the presence of the more toxic undissociated form of chlorophenol under acidic conditions (48, 50, 51, 93, 94, 95). Increased water hardness results in lowered toxicities of many environmental toxicants, although studies with chlorophenols are very limited.

Toxicity also increases with increasing chlorination of the chlorophenol molecule (96, 97). Therefore, DCP and TCP are usually less toxic than tetra- and pentachlorophenol. Much of the available information on toxicity relates to technical grade PCP which contains substantial quantities of impurities including chlorinated dibenzofurans, dibenzodioxins,

diphenyl ether and lower chlorinated phenols. Some studies have shown that significant differences exist between the toxicity of various PCP based compounds such as purified PCP, technical PCP formulations and commercial products such as Dowicide. Technical grade formulations usually have the highest toxicity, indicating that the impurities probably contribute significantly to the overall toxicity of the compound. Chronic exposure of fish to technical grade PCP results in yolk sac edema, degeneration of fins and opercles and cranial malformations not observed following exposure to purified PCP (85, 98).

4.2 Terrestrial Systems

4.2.1 Atmosphere.

General

The burning of chlorophenol contaminated wood wastes and railroad ties releases significant amounts of chlorinated phenols and toxic breakdown products, such as dioxins, to the atmosphere (103, 104, 105). Emissions from municipal incinerators have also been identified as an important source of these chemicals (106).

However, information on chlorophenol levels in the atmosphere and precipitation is very limited. Samples of rain collected near Burlington, Ontario in 1982 contained up to 10 ng/L PCP. Atmospheric concentrations of 5.7-7.8 ug PCP/1000 m^3 were detected in a residential area of Antwerp, Belgium compared to background levels of 0.25-0.95 ug/1000 m^3 detected in the mountains of La Paz, Bolivia at an elevation of 5200 feet (107).

A study in Portland, Oregon revealed that phenols in air samples are present mainly in the gaseous form. The average dissolved chlorophenol concentration for seven rain events were 22.6 ng/L T_4CP and 54 ng/L PCP, DCP and TCP were present at lower rates (108).

British Columbia

No information was available on chlorophenol levels in the air or precipitation of British Columbia.

4.2.2 Soil and Vegetation.

General

The presence of PCP and other chlorinated phenols in soils is normally attributed to spills, industrial releases, atmospheric transport, sewage application or leaching from treated wood products (fence posts, telephone poles).

Very few studies have examined the uptake of chlorophenols into vegetation from treated soils. A study on uptake of PCP from paddy soils indicated that, although low concentrations accumulated in rice plants, PCP was not persistent in the plants or in the soil (109). Pentachlorophenol and certain metabolites have also been detected in soybean and spinach plants grown on soil or sand containing 10 mg/kg PCP (110).

Mobility or transport of chlorophenols in soils and uptake into plants is dependent on the sorption capacity of the soil. Chlorophenols are more strongly adsorbed to soil with a low pH, fine particle size, and high organic matter and leaf litter content (18, 32, 33, 35).

Studies at wood preservative facilities in Finland demonstrated that a significant accumulation of chlorophenols (CPs), polychlorinated dibenzofurans (PCDFs) and polychlorinated phenoxyphenols (PCPPs) occurs in soils (CPs, 500-3500 mg/kg; PCDFs, 0.2 - 5 mg/kg; and PCPP, 1-50 mg/kg). Degradation products of chlorophenols (3,4-DCP and 3,4,5-TCP) were detected in soils, but there was no evidence of degradation of PCDFs or PCPPs. Unlike PCDFs and PCPPs, chlorophenols were mobile in soil and significant vertical leaching (>100 cm) into groundwaters was observed. In groundwater samples 2,3,4,6-T_4CP, 2,4,5-TCP and 2,3,4-TCP were commonly detected (111, 112). Soil samples from Finnish sawmills also contained polychlorophenoxyanisoles (PCPA), which are biomethylation products of PCPPs (113).

British Columbia

The only available information on chlorophenol levels in B.C. soils was obtained from industrial sites where spillage of wood preservative formulations had resulted in very high levels of contamination (several

hundreds of mg/kg). No information was available to indicate typical levels of chlorophenols in soils and vegetation from agricultural, urban or remote areas of the province.

B.C. Hydro and Environment Canada conducted studies to determine the leaching of PCP from hydro poles following groundline treatment with a preservative containing 10% PCP. Although significant PCP levels (up to 1700 ug/g at a distance of 10 cm) were detected in soils adjacent to the poles following treatment, minimal horizontal migration was observed (<1 to 122 ug/kg at distances of 1 metre or greater)(114, 115).

4.2.3 Wildlife.

General

Information on chlorophenol levels in wildlife species is very limited. Double-crested cormorant and herring gull eggs from a relatively pollution free area of New Brunswick contained 0.36 and 0.51 ug/kg PCP, respectively (116). Purple martin fledglings from central Alberta contained 31 ug/kg PCP and 2 ug/kg T_4CP (1). Sick and dead birds collected from Na-PCP treated rice fields in Surinam contained much higher PCP concentrations of up to 45.56 mg/kg in the liver, 20.34 mg/kg in the kidney and 11.25 mg/kg in the brain (117).

Low but detectable levels of chlorophenols have been detected in seals. Seals from eastern Finland contained PCP in all samples of blubber tested (0.23-1.0 mg/kg) and in two liver samples (0.06 and 0.11 mg/kg). T_4CP was present in two blubber samples (0.40 and 0.80 mg/kg) (118). Tissues from Hawaiian Monk seals contained much lower concentrations of PCP as follows: liver, 1.0 ug/kg; kidney, 0.8 ug/kg; blubber, 77 ug/kg; and urine, 66 ug/kg (119).

Accidental poisoning and contamination of livestock has occurred as a result of the use of treated wood shavings for bedding and building materials for fences and barns (1, 120, 121).

British Columbia

Information on chlorophenol levels in B.C. wildlife is very limited. Low ug/kg levels of T_4CP and PCP were detected in eggs from some

Lower Mainland heron colonies in 1983 by the Canadian Wildlife Service and Environmental Protection. Heron eggs collected in 1987 will be analyzed for chlorophenols.

CWS has also reported the presence of chorinated dibenzodioxins and dibenzofurans in heron eggs collected from several colonies in southwestern B.C. between 1982 and 1987 (122). The widespread use of chlorophenol for wood treatment in B.C. is a likely source of dioxins to the B.C. environment. The chlorine bleach process and the use of chlorophenol contaminated pulp at Kraft pulp mills are other potential sources of dioxin release.

Chlorophenols were also detected in the muscle (1.1 ug/kg PCP; 0.4 ug/kg T_4CP) and blood (9.1 ug/L PCP; 0.8 ug/L T_4CP) of a grey whale found dead in Semiahmoo Bay near White Rock. Chlorophenols were not detected in the blubber (39). The significance of these levels with respect to potential health effects on these animals is not known. However, these levels are much lower than those associated with toxic effects in terrestrial mammals.

4.2.3.1 Toxicity. There is no available information on the impact of present environmental levels of chlorophenols on wildlife populations. Documented incidents of accidental chlorophenol poisoning involve domestic and livestock animals.

Information on the toxicity of chlorophenols to mammalian and avian species has been obtained primarily from the controlled exposure of experimental animals. Symptoms of chlorophenol poisoning in experimentally exposed mammalian species include: increased blood pressure; fever; nausea; increased respiration; hyperglycemia; motor weakness; weakened eye reflex; glycosuria; convulsions; vascular system damage; congestion of lungs and certain other organs; internal hemorrhaging; and heart failure. Histological changes in the liver, kidney and spleen have also been observed (3, 123, 124, 125). Dermal exposure to PCP causes skin and eye irritation and severe acne like skin eruptions (123, 126).

It is possible that some of the toxic effects identified in birds and mammals following exposure to chlorophenols may actually be caused by the many impurities present in technical and commercial formulations. A wider range of toxic effects have been identified in animals exposed to technical grade chlorophenols than purified formulations, probably due to the presence of microcontaminants (123, 127, 128, 129, 130, 131).

Studies with laboratory animals indicate that at least some chlorophenols are fetotoxic, although there is no evidence that they are teratogenic (3, 126, 132, 133, 134, 135). Repeated dosages of 26-30 mg/kg purified PCP caused reductions in the number of offspring, neonatal survival and the growth of weanlings in rats. T_4CP caused similar effects at higher dosages (3, 131, 134, 135).

Laboratory tests for carcinogenicity indicate that 2,4,6-TCP may be a mammalian carcinogen but PCP is probably not (131, 136, 137).

Chlorophenols generally do not accumulate to high levels in mammalian tissues over the long term. All chlorophenols appear to be rapidly excreted, primarily in the urine. Conjugation with glucuronides has been reported in several species of experimental animals. Following exposure, the highest concentrations of PCP are normally detected in the liver (the main site of metabolism) and the kidney (the main organ of excretion) (3).

The toxicity of chlorophenols varies with a number of factors including the chlorination of the test compound; purity of the chlorophenol; formulation; and species and sex of the test organism.

LD_{50} values for rats exposed to lower chlorinated compounds ranged from approximately 250 to 3000 mg/kg body weight (123, 137); while LD_{50} values for tetra-and pentachlorophenol are usually in the 50-350 mg/kg body weight range. Females are typically more sensitive than males (123, 134, 135, 138, 139). In comparison, studies with calves have shown that dosages of 35-50 mg/kg PCP body weight over an 11 day period were lethal (140).

Chlorophenol toxicity also varies according to the route of exposure. Ingestion generally results in greater toxicity than dermal exposure but less toxicity than respiratory exposure.

5 REGULATIONS, GUIDELINES AND CRITERIA

The current regulations and guidelines pertaining to chlorophenols in the receiving environment are as follows:

5.1 Water Quality

The "Chemicals in the Environment" reports include environmental quality guidelines or criteria for these chemicals if such recommendations are available. Guidelines are provided for reference as one source of information in assessing environmental quality. It must be emphasized that guidelines must not be used in direct isolated comparisons with monitoring data. Site specific factors including local biophysical conditions must also be considered. For example, it must be recognized that guideline numbers may need to be modified to suit local aquatic conditions (e.g. toxicity of ammonia varies with pH, toxicity of many chemicals varies with presence of other toxicants, toxicity of most chemicals varies with species and life stage affected). Likewise, guidelines or criteria information cannot be used directly in formulating water quality objectives but requires consideration of site specific biophysical and socio-economic factors and requirements.

The Canadian Water Quality Guidelines were developed by the Canadian Council of Resource and Environment Ministers (CCREM) and were published in March 1987. The recommended guidelines for chlorophenols in fresh waters are: monochlorophenols, 7 ug/L; dichlorophenols, 0.2 ug/L; trichlorophenols, 18 ug/L; tetrachlorophenols, 1 ug/L; and pentachlorophenol, 0.5 ug/L (141). At present there are no Canadian water quality criteria or guidelines for acceptable concentrations of chlorophenols in marine waters.

The British Columbia Ministry of Environment is in the process of developing provincial criteria for chlorophenols in water, sediments and fish in freshwater systems.

The U.S. Environmental Protection Agency has published water quality criteria for several chlorophenols. These criteria have been designed for the protection of aquatic life and have been developed on an

individual chemical basis. The 1986 criteria for PCP specify a four day average concentration and a one hour average concentration that should not be exceeded more than once every three years. For saltwater systems the four day average concentration is 7.9 ug/L and the one hour average concentration is 13 ug/L. For freshwater systems the criteria are derived using a specific formula which incorporates the pH of the system (142).

5.2 Human Health

There are presently no Canadian guidelines for acceptable levels of chlorophenols in fish and shellfish for human consumption. Incidents of elevated chlorophenols in commercially important species would be reviewed on a case by case basis.

There are no existing Canadian drinking water guidelines for chlorophenols. However, the National Health and Welfare recommendation for a maximum acceptable concentration for phenolic compounds in water is 2 ug/L (143), based on the objectionable taste and odour characteristics of these compounds. This limit has been adopted in the British Columbia Drinking Water Quality Standards (144).

The World Health Organization recommended drinking water criteria for PCP is 10 ug/L (145).

5.3 Ocean Disposal

Acceptable levels of chlorophenols in materials destined for ocean disposal have been established under the Ocean Dumping Control Act. Chlorophenols are controlled under Schedule I of the Act which states that the maximum quantity or concentration of organohalogen compound in materials to be ocean disposed must not exceed "0.01 parts of the concentration shown to be toxic to marine animal and plant sensitive organisms in a bioassay sample and test carried out in accordance with procedures established or approved by the Minister". In the Pacific and Yukon Region a concentration of 1000 ug/kg is used as a guideline for acceptable levels of chlorophenol materials for ocean disposal.

5.4 Industrial Effluents and Emissions

Federal and provincial legislation provide controls on the entry of chlorophenols into the environment.

The federal Pest Control Products Act requires the registration of all chlorophenol products used, manufactured and sold in Canada. It also regulates chlorophenate products with respect to composition, packaging, labelling, distribution and use. The provincial Pesticide Control Act ensures that the sale and use of pesticides (including chlorophenates) in B.C. complies with label instructions.

The federal Fisheries Act subsection 33(2) prohibits the deposition of deleterious substances, such as chlorophenols, into waters frequented by fish. This legislation has been used to prosecute companies spilling chlorophenol concentrates or working solutions into B.C. freshwater or marine environments.

The British Columbia Waste Management Act controls the handling and disposal of industrial and municipal wastes. Regulations under this Act control the transportation and disposal of contaminated waste materials. Levels of chlorophenols in specific industrial effluents and atmospheric emissions can also be controlled under the provisions contained in this legislation.

The transport of chlorophenols and chlorophenol-contaminated wastes is regulated under the Transportation of Dangerous Goods Act (Canada). Regulations under this Act came into effect on July 1, 1985 and are administered jointly by the Federal and various Provincial and Territorial governments.

Environment Canada and B.C. Ministry of Environment and Parks, with input from both industry and labour, have published a set of detailed guidelines for the design and operation of sawmills and lumber export facilities using wood protection equipment. This publication, entitled "Chlorophenate Wood Protection - Recommendations for Design and Operation", will be undergoing revision in 1988. A similar set of guidelines is now being prepared for the wood preservation industry.

Environment Canada, Department of Fisheries and Oceans and B.C. Ministry of Environment and Parks are developing guidelines for allowable levels of antisapstain chemicals in stormwater discharges from wood protection facilities. These agencies have proposed a guideline of 10 ppb or less for chlorophenols. The Industry is currently reviewing the practical implications of the guideline and will comment by July, 1988. The guideline is scheduled to come into effect as of September 1, 1988.

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